



Screening of doped $\text{MnO}_x\text{--CeO}_2$ catalysts for low-temperature NO-SCR

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ABSTRACT

The effect of different dopants including niobium, iron, tungsten and zirconium oxide on the low-temperature activity of $\text{MnO}_x\text{--CeO}_2$ catalysts for the selective catalytic reduction (SCR) of NO_x with ammonia has been studied with coated cordierite monoliths in model gas experiments. A clearly higher activity and particularly superior nitrogen selectivity was obtained with the niobium-doped catalyst in comparison with the $\text{MnO}_x\text{--CeO}_2$ reference system. At 200 °C, the DeNO_x was 80% while the N_2 selectivity reached more than 96%. In contrast, a decrease of the SCR activity was observed when iron, zirconium or tungsten oxides were added to $\text{MnO}_x\text{--CeO}_2$. However, the addition of niobium oxide did not improve the resistance of the catalyst against SO_2 poisoning. A strong and irreversible deactivation occurred after exposure to SO_2 .

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1. Introduction

The selective catalytic reduction (SCR) with ammonia has been successfully applied for several decades to reduce NO_x emissions in the exhaust of stationary power plants, industry processes and recently also diesel vehicles [1–3]. However, one of the limitations for the application of the SCR process is the often insufficient activity of the commonly used vanadia- and zeolite-based catalysts at low temperatures, when NO_x mainly consists of NO. So far, different SCR catalysts have been shown to possess some activity for low-temperature NO-SCR. Most of the proposed catalytic systems contain transition metal oxides as catalytically active species [4–18]. Among several metal oxides, special attention is being paid to manganese oxide-containing systems. It has been shown that by deposition of manganese oxides on different supports, such as TiO_2 , CeO_2 , active carbon and Al_2O_3 , a significant enhancement of their activity is obtained. Recently, Qi and Yang [9,19,20] have reported very good NO-SCR activity and selectivity for the $\text{MnO}_x\text{--CeO}_2$ binary catalyst. Moreover, only a very low and reversible decrease of the SCR activity during exposure to SO_2 has been claimed for this system.

The remarkable low-temperature oxygen mobility gained by deposition of manganese oxides on ceria has already been observed in different oxidation reactions [21–23] and has been exploited also by our group for the low-temperature oxidation

reaction of diesel soot [24]. Our previous study [24] has shown that a considerable amount of NO_2 is formed by NO oxidation over $\text{MnO}_x\text{--CeO}_2$ already at low temperature. The resulting NO_2 is stored at the surface of the catalyst in the form of nitrates. However, we have also reported the high vulnerability to sulfur poisoning [24] and even a significant SO_2 storage capacity [25] for the $\text{MnO}_x\text{--CeO}_2$ catalyst, which is in contradiction to the findings of Qi and Yang [19,20]. The thermal stability of the formed sulfated species was very high and any attempt to regenerate the catalyst under oxidative or reductive atmosphere was unsuccessful. An irreversible destruction of the surface catalytic centers for the oxidation of NO to NO_2 occurred during the poisoning process [24].

These observations motivated us to systematically investigate the NO-SCR activity of $\text{MnO}_x\text{--CeO}_2$ as well as its sulfur poisoning behavior. Moreover, we carried out a screening of different $\text{MnO}_x\text{--CeO}_2$ -based catalysts for the NO-SCR reaction in the low-temperature region. Different redox active metal oxides, such as iron, niobium, zirconium and tungsten oxide, were added as potential promoters to $\text{MnO}_x\text{--CeO}_2$ and tested for the SCR performance, the NO oxidation to NO_2 , the selective catalytic oxidation (SCO) of NH_3 to N_2 and the SO_2 poisoning resistance in the temperature region of 100–450 °C.

2. Experimental

2.1. Catalyst preparation

The catalysts used in the present study were composed of manganese, cerium and another transition metal oxide as dopant

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(iron, tungsten, niobium or zirconium oxide) in a molar ratio of Mn:Dopant:Ce = 23:23:54. The samples were synthesized by dissolving the corresponding amounts of manganese acetate, cerium acetate and dopant precursor ($\text{Fe}(\text{NO}_3)_3$, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ and NbCl_5) in deionized water, followed by coprecipitation as hydroxides with an aqueous solution of NH_3 or $(\text{NH}_4)_2\text{CO}_3$. When NH_3 was used as the precipitant, a 3 M H_2O_2 solution was added to the suspension of metal hydroxides to complete the transfer of the metals from solution. Afterwards, the precipitate was filtered, washed with water, dried overnight at 120 °C and calcined in air at 650 °C for 5 h in ambient air. A dopant-free sample with a molar ratio of Mn:Ce = 30:70 was analogously prepared as reference catalyst.

The ZrO_2 -doped sample was prepared by the wet impregnation method (with an excess of liquid). A commercial $\text{CeO}_2\text{-ZrO}_2$ powder (Davicat CeZr 6201), containing 25 wt.% ZrO_2 , was added to an ammonia solution of $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$. In the next step, precipitation of MnO_2 was obtained with an excess of H_2O_2 . The resulting slurry was stirred for 1 h, dried at 120 °C and finally calcined at 650 °C in ambient air.

The catalysts were denoted as MnCe or MnXCe, where X = promotor element.

In order to evaluate the low-temperature SCR activity of the catalysts prepared in this study, a conventional $\text{V}_2\text{O}_5\text{/WO}_3\text{-TiO}_2$ catalyst containing 2.3 wt.% V_2O_5 , 8 wt.% WO_3 and TiO_2 prepared according to [26] was used as second reference material.

2.2. Catalytic tests

Prior to the measurements, 1.2–1.3 g of each catalyst powder were coated with a silica binder on small cordierite monoliths (3.8 cm × 1.7 cm × 1.2 cm) from Corning with a cell density of 400 cpsi according to a preparation procedure described elsewhere [26]. The thickness of the resulting coated layer was ~50 μm . The coated monoliths were calcined at 500 °C in air for 5 h.

A quartz plug flow reactor was used for the catalytic tests. The reactor consisted of a pre-heating zone filled with steatite pearls and a second heating zone for the monolith catalysts. Heating was accomplished with heating coils and the temperature was regulated by two thermocouples, positioned up- and downstream of the catalyst. To avoid bypasses of reacting gases, a ceramic fiber mat was used to fix the monolith in the reactor.

The model gas feed was composed of 10% O_2 , 5% H_2O , 0–1000 ppm NO, 0–2000 ppm NH_3 and balance N_2 . The effect of SO_2 on the NO_x removal activity was investigated by adding 50 ppm SO_2 to the feed gas mixture. The temperatures ranged from 100 to 450 °C at a gas hourly space velocity (GHSV = volumetric gas flow/coated monolith volume) of 52,000 h^{-1} , which is representative of the conditions in SCR converters on board of diesel vehicles. NO, NO_2 , N_2O and unreacted NH_3 were quantified with a high resolution Nicolet Magna – IR 560 FTIR spectrometer, with a detection limit of 3–5 ppm for NO_x and of 1 ppm for N_2O and NH_3 .

NO_x conversion (DeNO_x) was defined as follows:

$$\text{DeNO}_x = \frac{\text{NO}_{x,\text{IN}} - \text{NO}_{x,\text{OUT}}}{\text{NO}_{x,\text{IN}}} \quad (1)$$

where NO_x is the sum of NO and NO_2 concentrations.

When a mixture of NO and NO_2 was used, the DeNO_x due to the fast SCR reaction was calculated using the following equation [27]:

$$\text{DeNO}_{x,\text{fast}} = \frac{\text{NO}_{\text{IN}} - \text{NO}_{\text{OUT}}}{\text{NO}_{\text{IN}}} \quad (2)$$

Formal selectivities for the formation of N_2O , N_2 or NO_x during NH_3 oxidation were defined by the following relationships:

$$S_{\text{N}_2\text{O}} = \frac{C_{\text{N}_2\text{O}}}{C_{\text{NH}_3,\text{in}} - C_{\text{NH}_3,\text{out}}} \quad (3)$$

$$S_{\text{NO}_x} = \frac{C_{\text{NO}_x}}{C_{\text{NH}_3,\text{in}} - C_{\text{NH}_3,\text{out}}} \quad (4)$$

$$S_{\text{N}_2} = 1 - (S_{\text{NO}_x} + S_{\text{N}_2\text{O}}) \quad (5)$$

where $(C_{\text{NH}_3,\text{in}} - C_{\text{NH}_3,\text{out}})$ is the amount of converted ammonia and C_{NO_x} is the sum of NO and NO_2 concentration.

Although at low temperatures the absorption of both NH_3 and NO must be considered [2], on acidic SCR catalysts ammonia adsorption prevails, which justifies evaluation of the rate constant k_m assuming a first-order rate law with respect to the NO concentration:

$$k_m = -\frac{V^*}{W} \ln(1 - \text{DeNO}_x) \quad (6)$$

where k_m is the first order rate constant referred to the catalyst mass ($\text{cm}^3/\text{g s}$), V^* is the gas flow rate under reaction conditions (cm^3/s) and W is the active mass (g). This evaluation allowed us to compare our results with previous published data regarding the kinetics of the $\text{NH}_3\text{-SCR}$ reaction over $\text{MnO}_x\text{-CeO}_2$ -based catalysts as, e.g., in Ref. [20].

3. Results and discussion

3.1. $\text{MnO}_x\text{-CeO}_2$

The results of the SCR activity tests with the MnCe reference catalyst are presented in Fig. 1a. The measurements were performed with a gaseous mixture containing 1000 ppm NO, 1000 ppm NH_3 , 10% O_2 and 5% H_2O . For comparison, the NO_x removal efficiency (DeNO_x) of the conventional $\text{V}_2\text{O}_5\text{/WO}_3\text{-TiO}_2$ catalyst [26] is also shown (Fig. 1b). In the low-temperature region, the DeNO_x activity of MnCe was significantly higher than that of $\text{V}_2\text{O}_5\text{/WO}_3\text{-TiO}_2$, i.e., at 150 °C 24% of the NO_x could be reduced over MnCe but only 4% over the vanadium catalyst. This indicates that with a generously dimensioned MnCe catalyst ($\text{GHSV} \approx 10\text{--}15,000 \text{ h}^{-1}$) a DeNO_x of 60–70% could be achieved. Above 300 °C, the SCR activity of MnCe drastically decreased reaching even negative DeNO_x values due to the oxidation of ammonia to NO_x . Moreover, a major drawback of the MnCe catalyst is the very pronounced N_2O formation over the entire temperature window, increasing with temperature up to 300 °C and decreasing again at higher temperatures. In contrast, no evolution of N_2O was observed for the conventional vanadium catalyst below 450 °C. Above this temperature, the evolution of N_2O slowly starts.

The results of our work, regarding the SCR activity of the MnCe catalyst, are apparently in contradiction with some of the data already in the literature [19,20,28]. The data published by Qi and Yang [20] indicated a NO conversion of more than 80% at 80 °C, while at 120 °C almost 100% of the NO could be removed. Besides, only traces of N_2O were observed above 150 °C. Additional tests carried out in our laboratories confirmed that the lower performance observed during this study is due to the different measuring conditions and not caused by the different preparation methods of the catalysts (see electronic supplementary material). The main differences between this study and the data reported in literature are the presence of water in the model gas composition and the higher amount of catalyst used in our SCR tests. Since water is always present in the exhaust of combustion engines, its addition to the model gas feed is essential in order to investigate

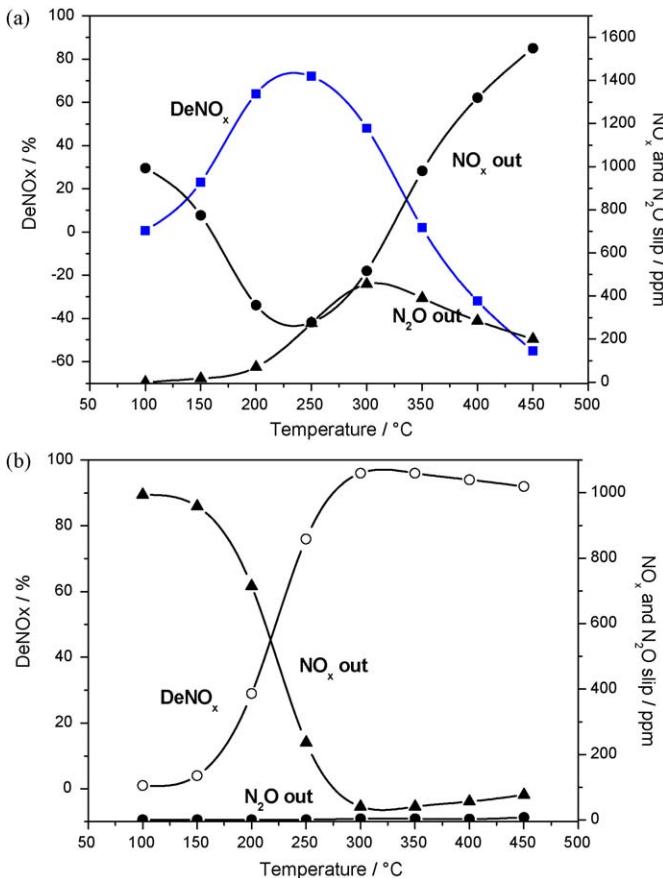


Fig. 1. SCR activity of (a) $\text{MnO}_x\text{-CeO}_2$ (■) and (b) $\text{V}_2\text{O}_5\text{/WO}_3\text{-TiO}_2$ (○) measured at different temperatures with a gaseous mixture containing 1000 ppm NO, 1000 ppm NH_3 , 10% O_2 , 5% H_2O and the balance was N_2 . The NO_x and N_2O slip are additionally depicted for both systems.

the real performance of the SCR catalysts. The GHSV is another important parameter for the assessment of the performance of a potential catalyst for NO_x removal. Contrary to the work of Qi and Yang [20] we determined the catalyst activities not on catalyst powders but on monolith catalysts with high catalyst loads similar to the situation in automotive catalysts. Complying with this constraint, approximately 1.2 g catalyst were typically coated on a monolith and tested at a GHSV of $52,000 \text{ h}^{-1}$ referring to the monolith volume. By contrast, only 0.2 g catalyst powder and a GHSV of $42,000 \text{ h}^{-1}$ referring to the powder volume were used for the experiments performed in [20]. Thus, in order to directly compare the catalysts activities, the measured DeNO_x and NH_3 oxidation values were converted into rate constants, k_m , which are independent of the space velocities. By means of this parameter, the influence of water was studied by repeating the SCR activity tests under dry conditions. These results are compared in Table 1, which includes the data reported in [20]. In the absence of water, the SCR activity of the MnCe catalyst prepared in our study is comparable to that observed by Qi and Yang [20]; however, the addition of 5% H_2O led to a strong decrease in the SCR activity. This finding is in accord with previous observations on other SCR catalysts for which the presence of H_2O inhibits the NO_x removal process [4,29–31] by competing with the adsorption of NH_3 on the reaction sites. The negative influence of H_2O on the catalytic activity of MnO_x -containing catalysts may originate from poisoning of the O-vacancies in MnO_x , as reported for the oxidation of CO [32,33]. However, water also has a positive impact on the SCR reaction by inhibiting the N_2O formation (Table 1). This effect is

Table 1

Reaction rate constants of the SCR reaction on $\text{MnO}_x\text{-CeO}_2$ in the presence or absence of water at different temperatures. The k_m values from Ref. [20] are listed as reference values.

Temperature (°C)	$\text{MnO}_x\text{-CeO}_2$			
	Without H_2O		5% H_2O	
	k_m (cm ³ /g s)	$S_{\text{N}_2\text{O}}$ (%)	k_m (cm ³ /g s)	$S_{\text{N}_2\text{O}}$ (%)
200	357	27	125	11
150	179	9	38	7
100	16	4	1	0
				Results from Ref. [20]
				k_m (cm ³ /g s)
				120.6
				40.5

explained by a two-step process. In the first step H_2O adsorbs stronger than N_2O and hydroxylates the surface of the catalyst. Thereafter, N_2O and hydroxyl groups react with each other in a dehydration reaction leading to the formation of N_2 [29,30,34].

Our results confirmed the promising SCR performance of manganese cerium mixed oxides in the low-temperature region. However, the still modest SCR activity and particularly the low selectivity of the catalyst require further improvement. For this purpose, an attempt was made to promote the MnCe-based system using a third metal oxide. The main criteria for the selection of the potential promoters were not only the catalytic properties, but also the non-toxicity and moderate price in view of a potential future application. The obtained ternary systems were systematically tested for their SCR activity and the main side reactions.

3.2. Catalyst screening

3.2.1. NO oxidation

The NO/NO_2 oxidation ability of the $\text{MnO}_x\text{-Dopant-CeO}_2$ catalysts was investigated as a function of the reaction temperature and the results are depicted in Fig. 2. The addition of the third component to MnCe led to a decrease of the NO conversion to NO_2 . The highest oxidation activity was observed in all cases in the range of 300–450 °C, at temperatures where the thermodynamic NO/NO_2 equilibrium is reached under high space velocity conditions. Among the doped catalysts, the highest performance was shown by the Nb_2O_5 and Fe_2O_3 containing catalysts. With

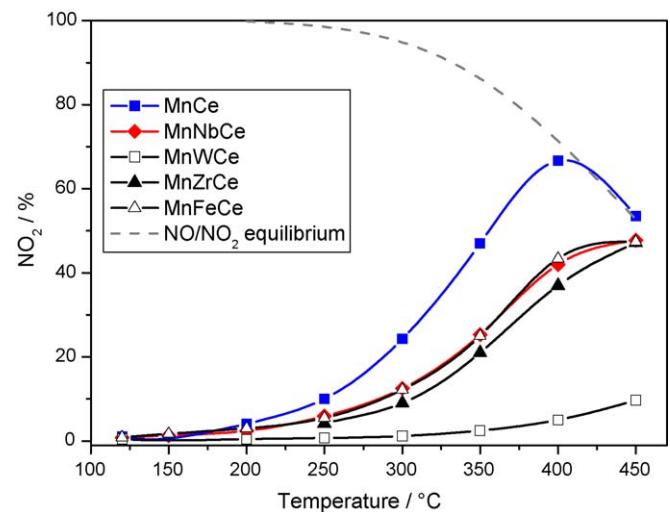


Fig. 2. NO oxidation to NO_2 as a function of temperature for various dopants. MnCe (■), MnNbCe (◆), MnWCe (□), MnZrCe (▲), MnFeCe (△). The feed was composed of 1000 ppm NO, 10% O_2 , 5% H_2O and the balance was N_2 .

these systems, ca. 47% of the NO species were oxidized to NO_2 at 400 °C. A similar activity was obtained for the MnZrCe catalyst. However, in the low-temperature region (150–250 °C), the NO/ NO_2 conversion on these catalysts was below 15%. A very modest NO to NO_2 oxidation was observed for the WO_3 -doped system over the entire temperature window.

3.2.2. NH_3 oxidation

Fig. 3a presents the selective catalytic oxidation of NH_3 on MnO_x -Dopant- CeO_2 as a function of the reaction temperature. Most catalysts showed excellent ammonia oxidation ability in the middle- and high-temperature region. However, beside N_2 also N_2O , NO and sometimes NO_2 were detected as products. At lower temperatures (200–300 °C), the activity of MnNbCe was slightly higher than that of MnCe. Its activity is combined with a very low selectivity to N_2O ($S_{\text{N}_2\text{O}}$ in Fig. 3b) and a very high selectivity to nitrogen (S_{N_2} in Fig. 3c). An even stronger suppression of the laughing gas formation was obtained with the MnWCe system, but this catalyst also showed a very low ammonia oxidation activity. On the other hand, MnFeCe and MnZrCe indeed showed high NH_3 oxidation activities above 250 °C, but significant amounts of N_2O were also formed.

3.2.3. SCR reaction

The DeNO_x activities measured for the doped catalysts are presented in Fig. 4. For comparison, the SCR activities achieved with the reference MnCe system and with a conventional V_2O_5 / WO_3 - TiO_2 catalyst have also been included. The significant influence of the dopant is obvious for the entire temperature window. At low temperatures (150–250 °C) the Nb_2O_5 containing catalyst showed the highest NO_x removal efficiency. Its performance was significantly higher compared to that of pure MnCe or the V_2O_5 -based catalyst. The addition of Nb_2O_5 to the MnCe catalyst resulted in a broadening of the activity temperature window towards higher temperatures. Moreover, the formation of N_2O was significantly lowered in the presence of Nb_2O_5 : the N_2O emissions were only 7 ppm at 150 °C and 86 ppm at 300 °C, whereas over MnO_x - CeO_2 17 and 455 ppm N_2O , respectively, were detected. Above 300 °C, the additional formation of NO_x by ammonia oxidation, as mentioned in Section 3.1, caused negative DeNO_x values. No significant promotional effect was observed with the other dopants. A drastic decrease of the SCR activity was measured when ZrO_2 and Fe_2O_3 were added to MnCe. With the W-containing catalyst, notable SCR activity was noticed only above 300 °C.

The obtained results show that among all tested dopants only the use of Nb_2O_5 leads to an enhancement of the NH_3 -SCR activity and simultaneously to a low N_2O formation. Niobium oxides are known to markedly increase the activity of different catalysts, mainly due to their acidic properties [35,36]. Since on all highly active SCR catalysts ammonia reacts from a strongly adsorbed state [37,38], any increase in the number of acidic sites will directly influence the activity of the catalyst. Preliminary experiments performed in our laboratories confirm that the increase in activity is not caused by a surface area stabilization effect [39], but by a significant enhancement of the surface acidity. Our observations are in line with the work of Weng and Lee [6] which demonstrated an increase in the number of acidic sites and thus, in the SCR activity, in response to Nb_2O_5 addition to a V_2O_5 - TiO_2 catalyst. These results will be discussed in detail in a future paper.

Nevertheless, the capability of MnNbCe to oxidize NO to NO_2 in the low-temperature range is low and may hamper the DeNO_x activity of the catalyst. In order to verify the eventual increase in activity in the presence of a higher NO_2 share, a feed gas containing 500 ppm NO and 500 ppm NO_2 was dosed to the catalyst and the

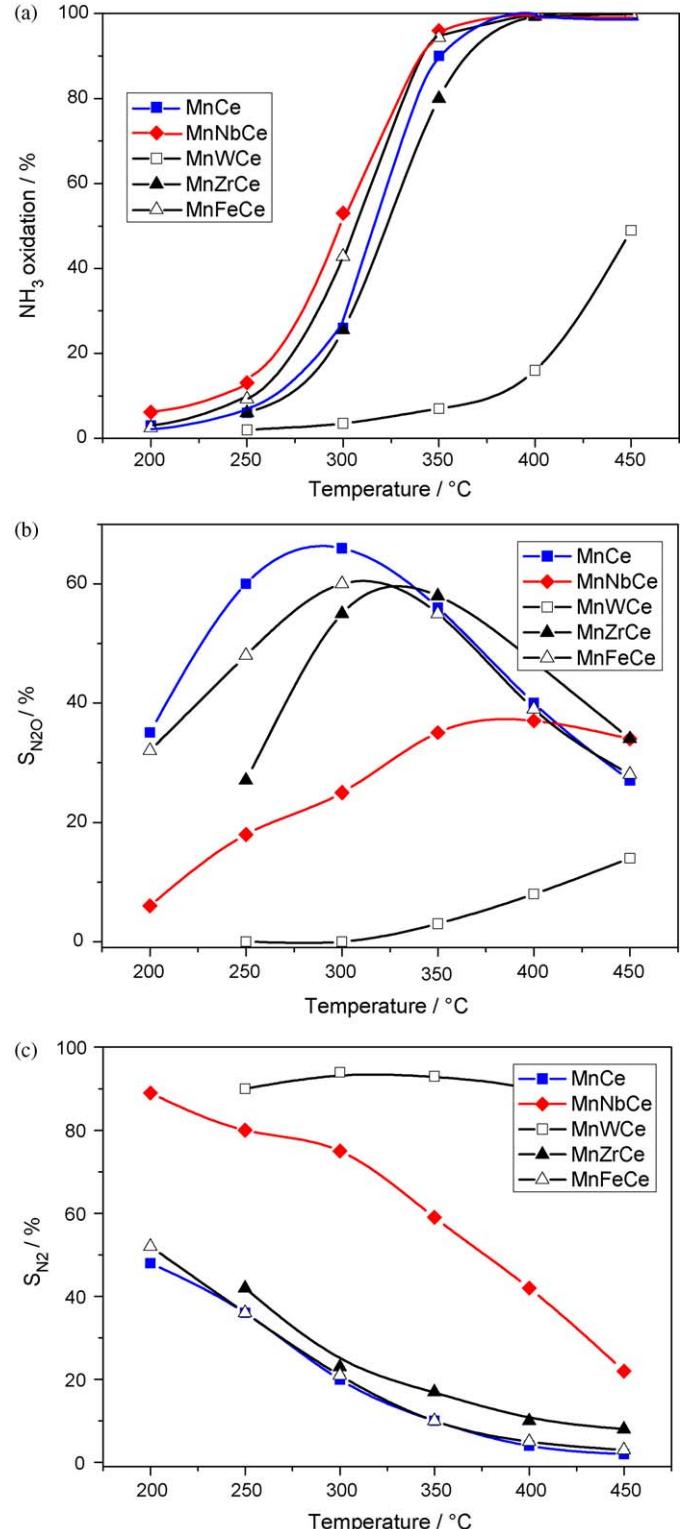


Fig. 3. Oxidation of NH_3 on the MnO_x - CeO_2 -Dopant catalysts vs. temperature. MnCe (■), MnNbCe (◆), MnWCe (□), MnZrCe (▲), MnFeCe (△). (a) NH_3 conversion, (b) selectivity for N_2O and (c) selectivity for N_2 .

activity was monitored between 120 and 200 °C. Since a practical application of the SCR process requires a high NO_x removal, but also a low ammonia slip, the amount of dosed NH_3 was varied between 0 and 2000 ppm in order to obtain a 10 ppm NH_3 slip which is regarded as harmless for automotive applications [40]. Fig. 5 shows the NO_x conversion at a 10 ppm NH_3 slip for a feed

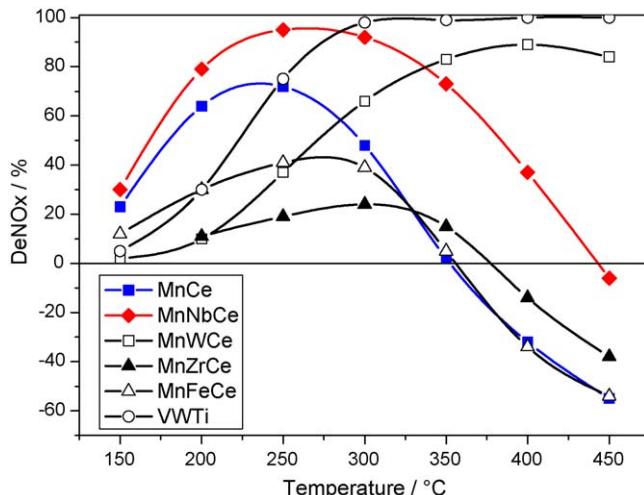


Fig. 4. DeNO_x activity of MnCe (■), MnNbCe (◆), MnWCe (□), MnZrCe (▲) and MnFeCe (△). The NO_x removal efficiency of VWTi (○) is also included for comparison.

with equimolar amounts of NO and NO₂ (500 ppm each). Since at temperatures below 200 °C the formation of NH₄NO₃ contributes to the measured DeNO_x values, we have subtracted the DeNO_x due to this competing process, as explained in [27], and included the DeNO_x values which are only due to the fast SCR reaction (DeNO_x,fast in Fig. 5). In order to compare these results with the corresponding experiment with only NO in the feed, the DeNO_x measured with 1000 ppm NO at a 10 ppm NH₃ slip is also shown in Fig. 5 for the temperature range of 150–350 °C. The observed N₂O concentrations are also included for each measured point. It can be seen from the results obtained in pure NO that above 200 °C DeNO_x reached values higher than 55%. When an equimolar mixture of NO and NO₂ was used, a very high low-temperature activity was measured for MnNbCe. At 150 °C, the NO_x removal due to the fast SCR reaction was higher than 83% (Fig. 5). However, with the NO–NO₂ feed, the N₂O formation became more pronounced compared to the experiment with only NO. At higher temperatures, where NO₂ was additionally generated on the catalyst surface, the selectivity towards N₂O formation increased above a reasonable

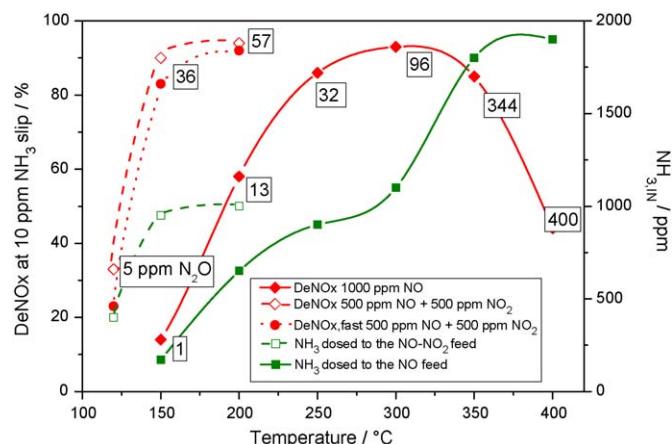


Fig. 5. DeNO_x at a 10 ppm NH₃ slip vs. temperature of MnNbCe catalyst in a feed containing 500 ppm NO to 500 ppm NO₂ (◊) or 1000 ppm NO (◆) and 10% O₂, 5% H₂O and N₂. The DeNO_x,fast which is due to the fast SCR reaction is also shown (●). The N₂O concentration is included for each measured point. The amount of the ammonia dosed to the NO–NO₂ (□) or to the NO (■) feed is additionally displayed.

limit. In summary it can be stated that, although the activity of MnNbCe increases with a NO–NO₂ feed, the other side reactions, such as NH₄NO₃ formation below 200 °C and N₂O formation at higher temperatures, question the application of NO–NO₂ mixtures for this type of catalyst.

3.2.4. Sulfur poisoning of MnNbCe

As mentioned above, previous results published by our group have demonstrated the poisoning effect of SO₂ for MnCe in the diesel soot oxidation reaction [24]. Moreover, it was shown that this effect may be exploited by using MnO_x–CeO₂ as an excellent SO₂ trap [25]. During SO₂ exposure, manganese sulfate, and not cerium sulfate, is preferentially formed since the manganese oxide protects the ceria against SO₂ poisoning [25,41].

In this study, the influence of sulfur poisoning on the SCR performance of MnNbCe and of the reference sample MnCe was investigated at 250 °C (temperature where the maximum NO_x conversion was observed) by adding for 30 min 50 ppm SO₂ to a feed containing 1000 ppm NO, 1000 ppm NH₃, 10% O₂, 5% H₂O and N₂. The results of these transient experiments are depicted in Fig. 6. Contrary to the work of Qi et al. [19], a drastic and irreversible decrease of the low-temperature DeNO_x activity was observed for

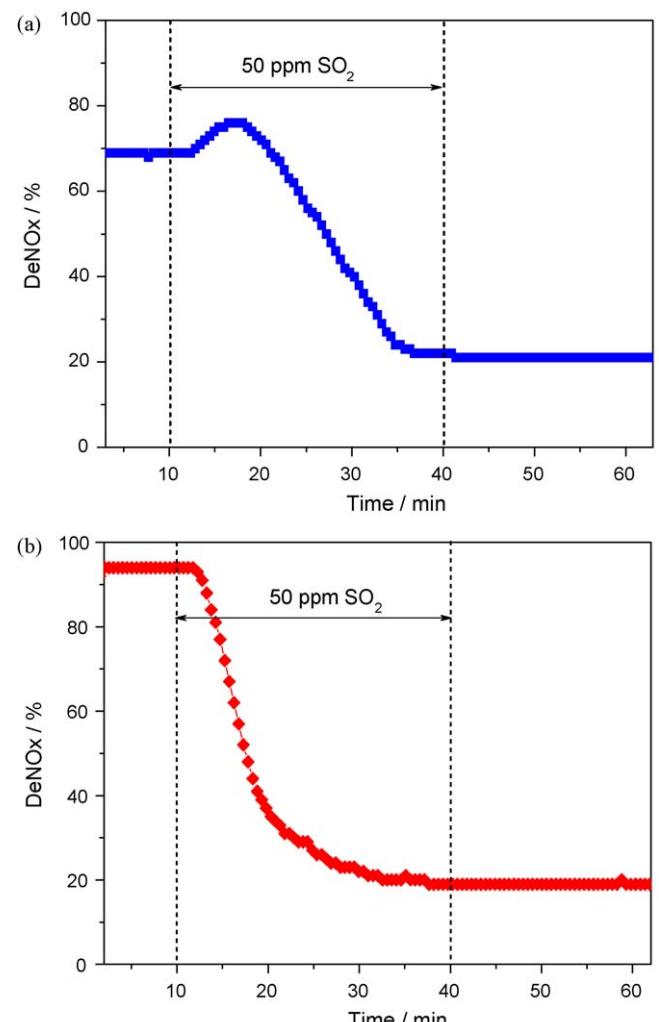


Fig. 6. SO₂ poisoning effect on the DeNO_x activity of (a) MnCe and (b) MnNbCe. Poisoning of the catalysts was performed at 250 °C for 30 min with a feed of 50 ppm SO₂, 1000 ppm NO, 1000 ppm NH₃, 10% O₂, 5% H₂O and N₂ balance. MnCe (■); MnNbCe (◆).

both catalysts which is in line with the high thermodynamic stability of manganese sulfate and our previous investigations on manganese cerium mixed oxides [4,5]. After a small and temporary increase of the DeNO_x , the catalytic activity of MnCe diminished with time and after 30 min reached ca. 20%. No recovery of the activity was measured after cutting off the SO_2 flow. The addition of Nb_2O_5 did not improve the resistance of MnCe to SO_2 poisoning. Also in this case, the DeNO_x dropped irreversibly below 20%. The small temporary increase of the DeNO_x activity, observed after the start of the SO_2 dosing to the MnCe sample, points to an increase of the catalyst surface acidity due to the formation of surface sulfates. After approximate 8 min, the sulfation advanced to the bulk species and as a consequence deactivation started (Fig. 6a). By contrast, the surface acidity of MnNbCe is already much higher than MnCe by the addition of acidic Nb_2O_5 , so that the start of SO_2 dosing either did not further increase the surface acidity or raises the surface acidity, but without any positive effect on DeNO_x , as optimum ammonia surface coverage is already achieved on MnNbCe without SO_2 dosing.

One may argue that the capability of the catalysts to oxidize SO_2 to SO_3 may lead to the formation of ammonium sulfate salts

(NH_4HSO_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_7$ and $(\text{NH}_4)_2\text{SO}_4$) in the presence of ammonia and water, which deposit on the catalyst surface and block the active sites. Such a process could add to the deactivation caused by the formation of manganese or cerium sulfate. However, when NH_3 was omitted in the feed the same degree of deactivation was found for MnCe and MnNbCe. Fig. 7 shows the results obtained when 50 ppm SO_2 were dosed to a feed containing only 10% O_2 , 5% H_2O and N_2 . In this experiment the impact of temperature on the sulfation degree (surface or bulk species) and particularly on the sulfates stability was checked by performing the SO_2 poisoning process at 100 and 350 °C. The results indicated that regardless of the sulfation temperature an irreversible loss of the activity occurred. Thus, the formation of stable metal sulfates seems to be the prevalent deactivation mechanism for both $\text{MnO}_x\text{--CeO}_2$ -based catalysts even at very low temperatures. However, it should be noted that the increase of the surface acidity by sulfate formation led to a significant enhancement of the DeNO_x above 350 °C. These observations are in accord with [42–45], where an increase of the SCR activity at very high temperatures was noted after SO_2 treatment. Additional NO/NO_2 oxidation activity tests performed with the SO_2 -treated MnCe and MnNbCe indicated that the SO_2 poisoning effect for the low-temperature SCR reaction arise due to the loss of the NO/NO_2 oxidation ability.

Since decomposition of the sulfated species occurred for both catalysts in the temperature range of 680–1100 °C (results not shown), an attempt was made to regenerate the catalyst poisoned at 200 °C by calcination in air for 2 h at 900 °C. Unfortunately, due to a very low thermal stability and strong sintering of both catalysts, a complete loss of the SCR activity over the entire temperature window (Fig. 7) was observed. The NO/NO_2 oxidative capacity of the catalysts could also not be restored by reduction with H_2 at 650 °C and by reoxidation at the same temperature, as shown in our previous investigation [24]. Therefore, the high SO_2 vulnerability observed for MnNbCe limits its applicability to sulfur-free processes or inclusion downstream of an SO_2 trap.

4. Conclusions

The basic study presented in this paper demonstrates once again the mandatory influence of the experimental conditions in assessing the performance of an SCR catalyst. Although the laboratory-scale activity measurement cannot perfectly mimic real exhaust gas conditions, the testing methods used during this investigation included the most important parameters. The SCR performance was not determined with catalyst powders but with catalyst-coated monoliths under realistic catalyst loads. The model gas feed contained the main components that are present in the exhaust of a combustion engine and was dosed to the catalysts at a realistic gas hourly space velocity.

The results obtained confirmed the promising DeNO_x activity of the $\text{MnO}_x\text{--CeO}_2$ system in the low-temperature region. However, its still modest activity and particularly low N_2 selectivity required additional improvement. Among different metal oxides doped to $\text{MnO}_x\text{--CeO}_2$, only the addition of Nb_2O_5 significantly increased the performance of the catalyst. A clearly superior activity and particularly N_2 selectivity was obtained with the MnNbCe catalyst in comparison to MnCe. At 200 °C, the DeNO_x was 80% while the N_2 selectivity reached more than 96%. The presence of NO_2 in the feed increased the activity of the catalyst at low temperatures but question the applicability window due to NH_4NO_3 and N_2O formation. Significant and irreversible loss of the low-temperature SCR activity was observed after sulfur poisoning for both MnCe and MnNbCe catalysts. Therefore, such a catalyst may be used only downstream of a desulfurizer or in a sulfur-free process.

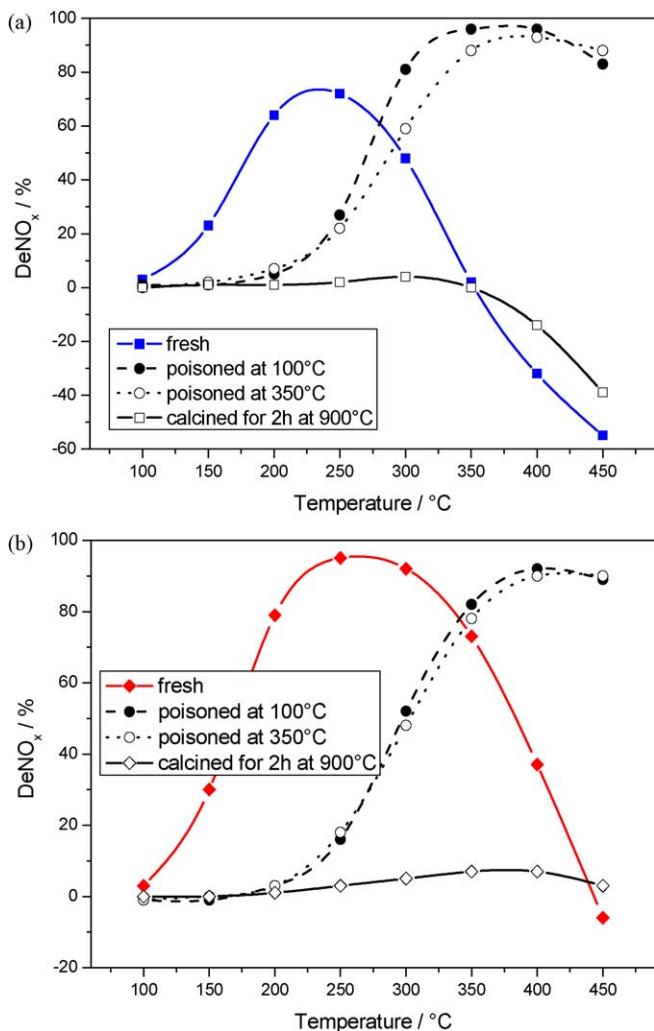


Fig. 7. SO_2 poisoning effect on the DeNO_x activity of (a) MnCe and (b) MnNbCe. Poisoning of the catalysts was performed for 30 min with a feed of 50 ppm SO_2 , 10% O_2 , 5% H_2O and N_2 balance. (a) Fresh MnCe (■), MnCe poisoned at 100 °C (●), MnCe poisoned at 350 °C (○), MnCe poisoned at 200 °C and calcined for 2 h at 900 °C (□). (b) Fresh MnNbCe (◆), MnNbCe poisoned at 100 °C (●), MnNbCe poisoned at 350 °C (○), MnNbCe poisoned at 200 °C and calcined for 2 h at 900 °C (◇).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2008.10.014.

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